Existence of Generalized Surface States

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Investigations of intrinsic surface states have been generalized beyond the nearly free-electron model. Simple conditions for the existence of surface states have been derived, and these results are presented. Detailed calculations have been made for transition metals, in particular for copper, and reveal that a substantial density of surface states (i.e., ~ 1 per surface atom) is a common occurrence.

It has been known for a number of years that electrons can exist in states localized near surfaces. The requirements are that (a) electrons have insufficient energy to escape into the vacuum, (b) they have momentum parallel to the surface and energy such that they encounter a band gap of the crystal and cannot escape into the bulk, and (c) wave functions can be matched at the surface to give a valid electron state. Surface states have received particular attention in connection with semiconductors because they strongly influence many properties of devices made from these materials.[1] Of more recent interest are the d-band surface states[2] occurring in gaps produced by hybridizing d bands, and it is with the latter that we shall be chiefly concerned in this Letter.

Two important questions may be asked. Firstly, can a simple criterion be found to decide whether a band gap will contain a surface state? Secondly, given that there is a surface state, at what energy does it occur, over what range of the two-dimensional Brillouin zone, and how is the charge distributed? For nearly free-electron (NFE) materials, such as silicon and germanium, the first question was answered by Shockley[3] for gaps at the zone boundary (surface states occur if the bands are "crossed," i.e., if the matrix elements put the p states at the bottom of the gap), and by Forstmann[2] for gaps in the center of the zone (surface states are always present in these gaps). Both results assume that the crystal potential extends unchanged to the surface plane lying halfway between layers of atoms, where the crystal is abruptly terminated. The second question has also been investigated for semiconductors[1] and some of the most comprehensive calculations are to appear shortly.[4] We have been able to provide some answers to these

questions in more general cases.

We begin with criteria for the existence of surface states. Since the algebra becomes involved, we shall describe only our conclusions. The details will appear in a later paper. The results were derived under the assumption that the band gap in question is sufficiently narrow that over its energy range all parameters not directly connected with the gap are essentially unchanged. It is also assumed that the surface has a mirror plane parallel to the surface in question. As in the NFE case, results differ for band gaps at a zone boundary and those inside the zone.

For gaps at the boundary, the generalization of the Shockley result is that the existence of a surface state again depends on the sign of the matrix element responsible for the gap. One sign of the matrix element gives a surface state, the other not, and which does depends on the details of the surface barrier. There is a 50% chance of a surface state at the zone boundary.

Forstmann's result for gaps away from the zone boundary generalizes to say that there is *always* a surface state, provided that any one of the following conditions is true: (a) The surface can be represented by an infinitely high square barrier truncating the perfect crystal at one of the mirror planes, (b) the hybridization responsible for the gap is caused by an interaction not present in the surface barrier, e.g., by spin-orbit splitting,[5] or (c) the hybridizing bands are free-electron-like. In the case that we have no information about the relevant parameters, assuming a random distribution gives a 70% chance of a surface state somewhere in the gap.

Other results from the theory are that there is only ever one surface state in gaps at the zone boundary, but in gaps away from both the zone

boundary and the zone center there can be up to two surface states.

So theoretical considerations lead us to believe that surface states are widely occurring phenomena and that wherever there is a suitable band gap we must suspect their existence. A detailed investigation of copper has been made, using the parametrized phase shifts of Cooper, Kreiger, and Segall,[6] which lead to a band structure essentially identical to that of Burdick.[7] The (100) surface was represented by a potential barrier, which was a function of the distance from the last plane of atoms only, the bulk crystal being truncated between atomic planes. The entire irreducible segment of the surface Brillouin zone was scanned using a step potential barrier placed midway between atomic planes. In addition, calculations were performed at respective points in the zone for several heights and positions of a square barrier to check the sensitivity of the results to these parameters, and also using a smooth potential barrier of the form $V = V_0(1 + e^{\alpha x})^{-1}$ at various positions and with various widths.

In this work no attempt was made at self-consistency of the charge density. Although we shall show that of the order of one electron per surface unit cell is present in surface states, this represents but a small fraction of the conduction electrons in copper, and readjustment to self-consistency will make only minor changes in our results.

To calculate the Bloch waves inside the crystal, the layer scattering method of Kambe[8] was

used. This requires as input parameters the energy and $k_\parallel$, the momentum parallel to a layer. This method is very convenient for surface calculations because it automatically generates precisely the Bloch waves we shall need. We can always decompose the crystal into layers parallel to the surface. The Bloch waves calculated were matched across the surface to decaying waves in the vacuum. For the calculations involving the step potential barrier this entailed a simple matching of wave function and derivative at the potential discontinuity. For the smooth potential barrier, the vacuum wave functions were integrated through the barrier and matched to the Bloch waves at a plane inside it. For energies and parallel momenta where no propagating bands exist in the crystal, the matching determinant may be made real by a suitable choice of phase for the wave functions. Thus we test for zeros in a real quantity to find a surface state.

The complete scan of the surface Brillouin zone was made using a step potential barrier placed half an atomic layer spacing from the first atomic layer. Its height, obtained by adding the experimental copper (100) work function to the Fermi energy (found by comparison with Burdick's results) was set at 0.47 hartree (27.2 eV = 1 hartree). The results are summarized in Figs. 1 and 2. A surface state was found to exist over about 70% of the surface zone, in general lying very close to the bottom of the gap. No states were found around $\overline{M}$ since there is no suitable gap in this region.

These surface states form a band 0.04 hartree wide, most of the states being in a peak of width 0.02 hartree. This peak is 0.19 hartree below the Fermi level. The average decay constant of the
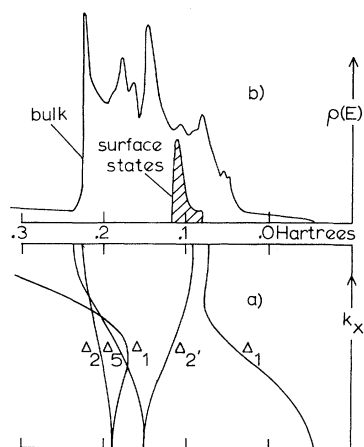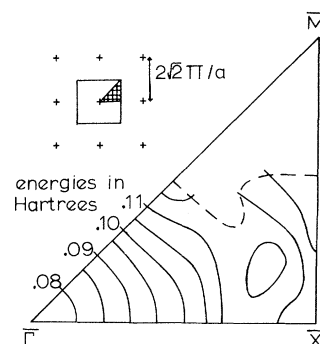

FIG. 1. (a) Band structure for copper normal to the (100) surface. (b) Density of surface states, as seen by a probe which penetrates into the first two layers only. The bulk density of states is shown for comparison.

FIG. 2. Irreducible part of the two-dimensional–surface Brillouin zone showing for what values of $k_\parallel$ a surface state exists on a (100) copper surface. Equal energy contours are marked. The inset shows the reciprocal net of the surface.

electron density in these states was calculated to be three atomic layers (~10 a.u.). Thus the peak density of electrons in localized states was about 40 electrons per hartree per atom in the first layer, compared to a bulk density of 40–50 in this energy region. The total number of electrons per atom in localized states, in the first layer, was 0.7.

At a few representative points in the surface zone, calculations were performed using a step potential barrier of various heights and positions. The surface states in the s-d gap were found to be insensitive to both these parameters, their energies shifting by less than 3×10^{-3} hartree for changes in barrier height of up to $\pm 20\%$ and barrier position by up to ± 0.3 interlayer spacings. This insensitivity to variations in the barrier leads us to expect that self-consistency does not play a key role in the existence of this surface state. However, states in the NFE gap (which is at the zone boundary, and is unoccupied in copper) were found to be very sensitive to the barrier parameters.

The results using a smooth barrier, at widths given by $\alpha = 2$ and 1.5 a.u.$^{-1}$ and positions chosen to give a reasonable approximation to the calculated surface potential,[9] showed similar behavior to those from the step barrier: The s-d gap states were insensitive, and the NFE zone-edge states sensitive, to the barrier parameters. These results for the NFE gap are similar to those found for various barrier widths in one dimension by Flores, Louis, and Rubio.[10]

Calculations have also been performed for the tungsten (100) surface. Except for $k_\parallel$ precisely equal to zero, there is no suitable gap, around $k_\parallel = 0$, but for higher $k_\parallel$ a gap opens and here a surface-state band was found to lie 0.16–0.24 hartree below E_F, the main peak being 0.03 hartree wide. The density of states and localization were quite similar to those in copper. In both cases the peak density was due to surface states with high $k_\parallel$. Our potential did not include spin-orbit coupling and therefore the spin-orbit gaps were not investigated.

We have shown that theoretical arguments suggest that surface states should be fairly widely occuring phenomena in d-band metal surfaces. In two particular, but typical, cases, tungsten and copper, we have performed numerical band calculations which show a band of surface states existing across a large part of the surface Brillouin zone in the s-d hybridization gap. Experimental evidence for surface states on d-band metals is scarce as yet, except for tungsten, where there is evidence of surface structure in both photoemission and field emission in the spin-orbit gap[11] and in photoemission in the s-d gap.[12] Surface states may be expected to have an important effect in the binding of adsorbates to the metal and in its catalytic properties. In the case of nickel (whose band structure is similar to that of copper, and which may, therefore, be expected to exhibit similar surface states) they may affect the magnetic properties of the surface. Thus, surface states on these metals seem to be worthy of further study, both theoretical and experimental.

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